AMERICAN MUSEUM NOVITATES

Number 759 Published by THE AMERICAN MUSEUM OF NATURAL HISTORY New York City Dec. 20, 1934

54.8, 5

MINERAL INCRUSTATIONS UPON THE EDGES AND CORNERS OF CRYSTALS

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ABSTRACT

Instances are described of mineral incrustations confined to the edges or corners of the incrusted crystals. The effect is explained by the greater adsorptive power of these portions of the crystal surface. Adsorption by the edges and corners of growing crystals may be accompanied by a change in crystal habit, modifying faces being developed which suppress the adsorbing edge or corner.

PROPERTIES OF THE EDGES AND CORNERS OF CRYSTALS

The crystallization of one mineral upon another in the formation of a mineral incrustation is in general influenced by adsorption at the crystal—solution interface. Adsorption control of the super-crystallization may be manifested by the formation of an oriented incrustation; by the selective incrustation of a particular form of the incrusted crystal,[1] owing to the varying adsorptive power of different crystallographic directions; by the selective incrustation of one of several mineral species whose free crystals are exposed in an opening and are available for incrustation by a later formed mineral; and by the formation of incrustations localized to the edges or corners of the incrusted crystal.

The greater adsorptive power of the edges and corners of crystals as reflected by their ability to localize the crystallization of a substance upon them can be illustrated by experimental means. Edge incrustations of sodium nitrate upon calcite can be readily obtained by crystallizing a sodium nitrate solution upon freshly cleaved fragments of calcite. The sodium nitrate forms rhombohedrons disposed in parallel position along the edges of the calcite cleavage pieces. A paper by Bombicci[2] on the parallel growths formed by these two isomorphous substances contains twenty-odd figures which clearly illustrate the effect of the edges in localizing crystallization. The effect has also been re-

[1]Frondel, C. 1934. Amer. Min., XIX, pp. 316–329.
1934. Amer. Mus. Novitates, No. 695, pp 1–6.
[2]Bombicci, L. 1876. Mem. Accad. Sci. Inst. Bologna, Ser. 3, VII, p. 125.

marked on by Settele.[1] Similarly when sodium chloride is crystallized upon a fresh cleavage section of galena, the crystals may be observed to be aligned in parallel position along cleavage cracks or tear-lines on the cleavage surface.[2] A parallel alignment of sodium bromide crystals along the edges of cracks on a galena cleavage surface has also been figured[3]. Certain natural galena crystals contain small cavities filled with a sodium chloride solution, and when these crystals are cleaved, the solution spreads and crystallizes, producing lines of small halite crystals disposed in parallel position along curved tear-lines on the cleavage surface. Photographs of these edge growths have been published by Buerger[4] and by Head.[5] The crystallization of iodine from vapor has also been observed to be influenced by striations and rugosities on the condensing surface.[6]

Seemingly related to these occurrences are those in which the crystallization of a solution is initiated or localized by the scratching of the containing vessel. The effect is particularly well marked with ammonium magnesium phosphate and similar Mg salts and was early considered by Wollaston to be a test for Mg[7]. The crystallization of metastable forms may sometimes be induced in this way.[8]

Schwab and Pietsch[9] have shown by a photographic method that the adsorption of radio-elements by crocoite does not occur over the whole surface but takes place principally along the edges of the crystal. The use of certain aniline dyes in microchemical determinative methods based on the selective staining of the minerals of rock sections is limited by their tendency to indiscriminately stain rugosities and cracks on the section. This also appears to be an instance of edge and corner adsorption. An instance of edge and corner adsorption by a growing crystal of lead nitrate accompanied by habit change has been described by Gaubert.[10] This substance crystallizes as octahedrons from a pure water solution and as cubes from a solution containing methylene blue. When octahedrons are placed in a super-saturated solution containing methylene blue, the dye is adsorbed by the crystal corners and edges adjacent to the corners, hindering growth in these directions, and cubes are produced by overgrowth. Summaries of further evidence from many

[1]Settele, M. 1930. Neues Jahrb. Min., Abt. A, Beil.-Bd. LXI, p. 227.
[2]Sloat, C. A., and Menzies, A. W. C. 1931. Jour. Phys. Chem., XXXV, p. 2006, Pl. 1.
[3]Grimm, H. G. 1924. Zeits. Elektrochem., XXX, p. 469, fig. 4.
[4]Buerger, M. J. 1932. Amer. Min., XVII, p. 228, fig. 1.
[5]Head, R. E. 1931. Amer. Min., XVI, p. 349, fig. 3.
[6]Wulff, J. 1929. Zeits. phys. Chem., Abt. B, VI, p. 43.
[7]Waller, A. 1846. Phil. Mag., XXVIII, p. 94.
[8]Gernez, D. 1877. Compt. rend., LXXXIV, pp. 1389-1392.
[9]Schwab, G. M., and Pietsch, E. 1929. Zeits. phys. Chem., Abt. B, II, pp. 262–263.
[10]Gaubert, P. 1926. Revue gen. sci., XXXVII, p. 365.

diverse branches testifying to the greater adsorptive power of the edges and corners of crystalline substances are given by Frazer[1] and by Schwab and Pietsch.[2] The development of the subject is largely owing to workers in contact catalysis.

The effect of the edges and corners is accounted for in a theory proposed by Taylor,[3] which follows. The atoms composing a crystal surface are in varying degrees of saturation according to the degree to which their external fields are saturated by surrounding atoms. Atoms situated in a plane surface will have a certain degree of saturation on the free side. Those situated in the edges of the crystal will be one degree less saturated than the atoms in the plane surfaces, by reason of the fact that they are to a less degree surrounded by other atoms. For this reason the edges will possess stronger attractive forces for impinging atoms. This increased attractive force at an edge will be surpassed by that obtaining at a corner. The localization of the super-crystallization to the edges in the experimental examples mentioned is thus due to the adsorption of substance from solution on them to a greater degree than on the adjacent plane surfaces. This favors the formation of crystal nuclei upon them with the inception of crystallization. The edge and corner incrustations involving natural species to be described are similarly believed to be of this origin, with the possible exception of certain pyrite and marcasite incrustations upon calcite in which the deposition may have been controlled by chemical reaction with the incrusted crystal, the greater rate of solution of the edges acting to localize the deposition, and with the further exception of instances in which colloidal particles seem to have been directly adsorbed by the edges of the crystals.

The edges and corners of crystals are also distinguished in other ways. The greater rate of solution and more rapid growth of these portions of the crystal surface are well known. The edges are usually simply rounded off by solution but the action of the solvent sometimes results in the formation of narrow grooves or indentations along the crystal edges, as with quartz[4] and pyrite.[5] Raised edges are commonly observed on natural and artificial crystals of gold and other metals and also on quartz, galena and other species. Overgrowths of successive generations of different habit of a mineral frequently initiate upon the corners of the earlier crystals, as is notably the case with fluorite. The

[1]Frazer, J. W. C. 1930. Jour. Phys. Chem., XXXIV, pp. 2133–2136.
[2]Schwab, G. M., and Pietsch, E. 1929. Zeits. Elektrochem., XXXV, pp. 573–582.
[3]Taylor, H. S. 1925. Proc. Royal Soc. London, CVIII, A, pp. 105–111. 1926. Jour. Phys. Chem., XXX, p. 150.
[4]Ichikawa, S. 1915. Amer. Jour. Sci., Ser. 4, XXXIX, p. 455.
[5]Ichikawa, S. 1929. Amer. Jour. Sci., Ser. 5, XVII, p. 251.

rough fracture surfaces of crystals yield more readily to solution than do the natural faces and are healed more rapidly during growth.

Experiments have been described[1] which have shown that certain chemical reactions take place more readily on the edges of crystals than over the plane surfaces. The localization of the reaction is due to the greater rate of solution of the edges rather than to adsorption. It is similarly found that bubbles of CO_2 appear chiefly along the edges and corners of alum crystals when they are immersed in solutions of carbonates. Crystals of sodium alum effloresce on the edges.

DESCRIPTION OF SPECIMENS[2]

Dolomite Incrusting Rhodochrosite

An oriented edge and corner incrustation of dolomite upon rhodochrosite very similar to the experimentally obtained edge incrustations of sodium nitrate upon calcite is shown by two specimens from the John Reed Mine, Alicante, Lake Co., Colorado. The rhodochrosite crystals are pale rose-red individuals composed of $(10\bar{1}1)$ and form druses in cavernous vein material. On one specimen rhodochrosite rhombohedrons up to 1 cm. on an edge are incrusted by minute (.5 mm.) dolomite rhombohedrons with a vitreous pearly appearance which are aligned in parallel position along the edges of the crystals, the faces themselves being free from deposition. On a number of the rhodochrosite crystals of this specimen the corners only are incrusted by the dolomite (Fig. 1); other crystals showed corner incrustations with one or two smaller isolated dolomite crystals disposed along the edges themselves. The second specimen is similar, but the dolomite crystals are slightly larger and are aggregated to form a continuous ridge along the edges of the incrusted crystals (Fig. 2).

The oriented growth of dolomite upon rhodochrosite has not been previously described.

Fluorite Incrusting Calcite

J. L. Smith[3] has described groups of calcite crystals of a scalenohedral habit from the Wheatley Mine, Chester Co., Pennsylvania, the apice of each crystal of which is tipped by a small crystal of fluorite, the remaining portions of the crystals being unincrusted. These crystals with their incrustation were overgrown during or after the crystalliza-

[1] Pietsch, E. Kotowski, A., and Berend, G. 1929. Zeits. Elektrochem., XXXV, pp 582-586.

[2] The specimens described are contained in the collection of The American Museum of Natural History, unless otherwise stated.

[3] Smith, J. L 1855. Amer. Jour. Sci., Ser. 2, XX, p 252, fig. 4.

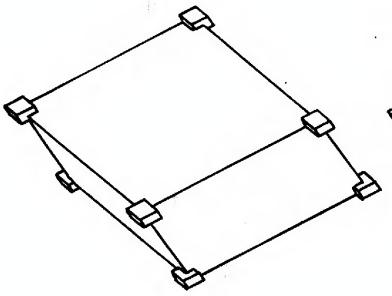

Fig .1

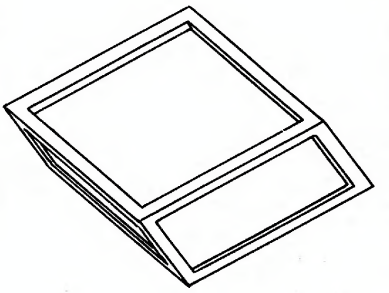

Fig. 2

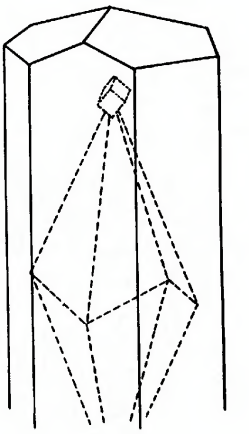

Fig. 3

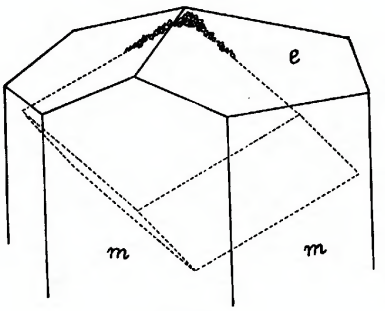

Fig. 4

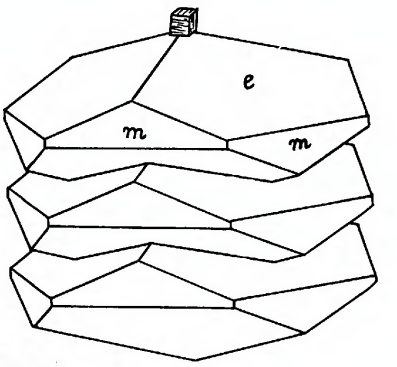

Fig. 5

Figs. 1, 2. Dolomite incrusting in parallel position the corners and edges of rhodochrosite. John Reed Mine, Alicante, Colorado.

Fig. 3. Fluorite tipping a calcite scalenohedron enclosed within an overgrowing crystal of different habit. Wheatley Mine, Chester Co., Pennsylvania.

Fig. 4. Marcasite incrusting the edges of a $(10\bar{1}1)$ crystal of calcite that has been enclosed by overgrowth within a crystal formed of $(10\bar{1}0)$ and $(01\bar{1}2)$. Przibram, Bohemia.

Fig. 5. Pyrite tipping the apice of a composite calcite crystal formed of $(10\bar{1}0)$ and $(01\bar{1}2)$. The lower, overgrown, crystals are also tipped by pyrite. Przibram, Bohemia.

tion of the fluorite by calcite of a different habit (Fig. 3). Smith does not give the identity of the forms present on the crystals, but his figure, copied here, apparently consists of $(21\bar{3}1)$ with $(10\bar{1}0)$ and $(01\bar{1}2)$ as the habit of the overgrowing calcite. It is not remarked if the fluorite is crystallographically oriented to the calcite but this does not appear to be the case.

Marcasite Incrusting Calcite

A specimen of calcite from Przibram, Bohemia, presents a group of $(10\bar{1}1)$ rhombohedrons attached by one end of their vertical axis to the matrix with the exposed apice of the crystals, that is, the corner of the trihedral angle formed by $(10\bar{1}1)$, $(\bar{1}101)$ and $(0\bar{1}11)$, and the edges for a short distance away from the apice heavily incrusted by an aggregate of small platy crystals of marcasite. The middle edges and corners of the rhombohedrons and the faces themselves are free from incrustation. During or after the formation of the incrustation the crystals were overgrown by calcite that formed crystals composed of $(10\bar{1}0)$ and $(01\bar{1}2)$ (Fig. 4). The rhombohedrons range in size up to 1 cm. and the enclosing crystals are only slightly larger. The marcasite incrustation in part slightly projects above the surface of the later crystals.

Pyrite Incrusting Calcite

Przibram, Bohemia

An extraordinary example of corner incrustation is afforded by two specimens from the Anna Mine, Przibram, Bohemia, which present drusy surfaces of thin tabular calcite crystals composed of $(01\bar{1}2)$ modified by $(10\bar{1}0)$ with the apice of each crystal tipped by a minute cube of pyrite (Fig. 5). The other corners and edges on the crystals and the faces themselves are entirely free from pyrite. The calcite crystals uniformly measure about 2 mm. across and have grown so that the vertical axis is approximately perpendicular to the incrusted wall rock. About 500 crystals are present on the two specimens and the incrustation is lacking from only about 50 of these. The great majority of the pyrite crystals are minute, the largest one seen measuring .3 mm. on an edge. Many of them consist of two or three closely interpenetrating individuals. Occasionally a considerable number of minute pyrite crystals are aggregated together and in these cases the pyrite mass extends from the apice down the edges of $(01\bar{1}2)$ for a short distance. When single crystals of pyrite occur perched upon the calcite apice it can be seen that the two minerals are not definitely oriented to each other.

The calcite crystals frequently occur piled one on top of another, sometimes in alignment and forming a single but strongly composite crystal, as in Fig. 5, but generally in a random overlapping pile and it can be seen in such cases that each of the calcite crystals has a pyrite cube perched upon its summit. Sometimes six or seven calcite crystals, all of equal size, occur heaped up in this way, each covering an earlier pyrite-incrusted crystal. This behavior suggests periodicity in deposition.

Locality Unknown

A photograph of a group of rhombohedral calcite crystals with the corners and part of the edges adjacent to the corners heavily incrusted by pyrite has been published by Schwab and Pietsch[1] in connection with their discussion of adsorption by the edges and corners of crystals. The specimen is not described and the locality is not stated.

Rondout, New York

Whitlock[2] has described calcite from Rondout, Ulster Co., New York, in which the edges of crystals composed of $(10\bar{1}1)$ have been incrusted by an aggregate of minute crystals of pyrite. These crystals are overgrown by calcite crystals formed of $(01\bar{1}2)$ with $(31\bar{4}2)$ and $(10.3.\overline{13}.2)$ which preserve the incrusted crystals in their interior.

Rand, South Africa

Young[3] has noted that calcite crystals occurring in drusy cavities in veins cutting the Main Reef series in the Rand, South Africa, contain innumerable crystals of pyrite in their outer portions, giving the calcite a greenish tint, which have "very evidently been precipitated by preference on the edges and corners of the crystals."

Wheatley Mine, Pennsylvania

Edge incrustations of pyrite upon calcite have been described by Smith[4] from the Wheatley Mine, Chester Co., Penn., where they are found with the corner incrustations of fluorite upon calcite already mentioned. The occurrence is similar to the edge incrustation of marcasite upon calcite from Przibram, described earlier, in that calcite crystals formed of $(10\bar{1}1)$ were incrusted along the edges by minute crystals of pyrite, and these crystals with their incrustation were then enclosed in

[1]Schwab, G. M., and Pietsch, E., op. cit., fig. 4.
[2]Whitlock, H. P. 1910. N. Y. State Mus. Mem. 13, p. 124, Pl. XXVII, fig. 3.
[3]Young, R. B. 1910. Trans. Geol. Soc. South Africa, XII, p. 93.
[4]Smith, J. L., op. cit., fig. 6.

slightly larger calcite crystals of a habit dominantly formed by $(10\bar{1}0)$ and $(01\bar{1}2)$.

Smith further notes from this locality pyrite incrustations upon calcite which seem to represent a selective incrustation of the forms of a calcite crystal enclosed in a larger crystal of later growth[1] and also describes a singular aggregation of a large number of calcite crystals in the form of a closed double spiral, as if around an axis.

The localization of the sulphide incrustation to the edges and corners of the incrusted crystal in this and in the preceding instances and in the edge incrustation of marcasite upon calcite may possibly have resulted from the chemical reaction of the calcite with the sulphide solution, the greater rate of solution of the edges and corners of the crystals acting to localize the sulphide deposition. The absence of visible solution effects on the crystals studied at first hand, however, and the simultaneous deposition of the sulphide and the carbonate in the instances described from Przibram and the Rand and probably also in the instances accompanied by overgrowth, point to the adsorption by and simple crystallization upon the calcite by the sulphide. Marcasite has been described as being syncrystallized with calcite,[2] although marcasite ordinarily crystallizes from acid solutions in which calcite would be soluble, and pyrite and other sulphides are often found so.

Tetrahedrite and Chalcopyrite Incrusting Sphalerite

A group of nearly black crystals of sphalerite from Butte, Montana, presents distorted tetrahedrons repeatedly twinned on (111) with the edges of the crystals and the edges of the re-entrant angles formed by the twins marked by rows of minute tetrahedrite crystals in parallel alignment. On some crystals, ten or more parallel rows of tetrahedrite crystals are developed along the edges of the twinned lamellae. Triangular striations formed by terrace-like growth hillocks on the faces of the tetrahedrons are also occasionally outlined by rows of minute tetrahedrite crystals.

A suite of specimens from an unknown locality in the western United States presents successive incrustations of galena, sphalerite and tetrahedrite upon very large distorted crystals of chalcopyrite. The sphalerite for the most part forms large nearly transparent yellow green crystals

[1] An incrustation of pyrite selective upon the forms of a calcite crystal has been described by J. D. Dana (1844, System of Min., 2d Ed., p. 93).

[2] Brewster, D. 1864. Trans. Royal Soc. Edinburgh, XXIII, p. 98.
Whitlock, H. P. 1910. N Y. State Mus. Mem. 13, p. 106.
Lindgren, W. 1915. U. S. Geol. Surv. Bull. 601, p. 45.
Merwin, H. E. 1914. Amer. Jour. Sci., Ser. 4, XXXVIII, pp. 355-359.
Frondel, C. 1934. Amer. Mus. Nat. Hist. Novitates, No. 695, pp. 5–6.

which have overgrown the chalcopyrite and the galena. The tetrahedrite, which was the last mineral to crystallize, forms small, sharply defined crystals that are markedly arranged, in parallel position, along striations formed by twinning and by vicinal growth on the surface of the sphalerite. A very minor amount of chalcopyrite crystallized out with the tetrahedrite and is similarly disposed along the striations. This later generation of chalcopyrite forms dull rough surfaces and rows which appear to the eye as consisting of irregular grains, but when such aggregates are viewed from certain angles, a satin-like sheen is seen which is due to a parallel orientation of minute crystal faces on the grains.

The galena, sphalerite and tetrahedrite in part occur as small isolated crystals situated on the early formed chalcopyrite crystals. The galena and the tetrahedrite are oriented to that species but the sphalerite is not. The galena forms cubo-octahedrons with (111) in contact with (111) of the chalcopyrite and with the crystal axes of the two minerals parallel to each other. The chalcopyrite is strongly striated but the distribution of the incrustation is not noticeably influenced by these edges or by the ordinary edges and corners of the crystals.

Tetrahedrite Incrusting Chalcopyrite

An edge incrustation of tetrahedrite upon chalcopyrite crystals, although not a striking one because of the small number of tetrahedrite crystals present, was observed on a specimen from Central City, Gilpin Co., Colorado. The chalcopyrite forms a large group of untarnished and strongly striated sphenoids, averaging 1 cm. in size, incrusting a matrix of quartz and pyrite. An oriented incrustation of tetrahedrite in small isolated crystals is present upon a few of the chalcopyrite crystals and is for the most part distributed along the edges of these and in a few instances is situated directly upon the corners.

Sadebeck[1] has described an oriented incrustation of tetrahedrite upon twinned "fivelings" of chalcopyrite from Meiseberg, Saxony, which is largely developed upon the corners of the incrusted crystals.

Hematite Incrusting Calcite

Instances of edge adsorption by calcite crystals are found which differ from the previously described instances in that the deposited substance appears to have been directly adsorbed as colloidal particles from a sol which enveloped the crystals during or after their growth.

Complexly developed calcite crystals from West Paterson, N. J.,

[1]Sadebeck, A. 1872. Zeits. deutsch. geol. Ges., XXIV, p. 441, figs. 18, 19.

have been described on which the faces of a particular form are covered by a rose-red or rose-colored film of hematite which was adsorbed selectively by that form from an iron oxide sol which bathed the crystals at some time after the completion of their growth.[1] The edges of these filmed faces are strongly marked by a deep red line of hematite, the other edges of the crystal not being thus marked, and this edge deposition seems to represent the initial stage of formation of the film. On some crystals only the edges of these faces have received deposition, although then but slightly, while the faces themselves are unfilmed.

Three specimens of calcite from localities in Lancashire, England, present groups of crystals of a modified scalenohedral habit which contain inner scalenohedral crystals of calcite the edges of which are outlined by pulverulent hematite.[2] The hematite coating is not strictly confined to the crystal edges but is most dense there and rapidly decreases in intensity towards the interior of the faces. The coating is particularly heavy towards the apical part of the crystals. The habit of the inner, coated crystals in these instances is formed by simple $(21\bar{3}1)$ scalenohedrons. The overgrowing calcite differs in habit from this and forms crystals dominantly composed of $(21\bar{3}1)$ with small rounded and striated modifying faces of $(10\bar{1}1)$ and $(01\bar{1}2)$ in one of the instances and these two modifying forms with $(13\bar{4}1)$ also in the two other instances.

Calcite crystals showing inner crystals delineated by hematite or by a flocculent black substance were observed on a number of specimens from Cumberland, Derbyshire, Lancashire and other localities but without the feature of edge deposition described. Woodward[3] has catalogued calcite from a locality near Haddon, Derbyshire, as "Two Pieces of a pellucid Spar lineated with black in such manner, as to shew the Order and Succession of the Matter in the Formation of the Mass."

It is of interest to note that the habit change in these and in the previously described instances of calcite overgrowth accompanying an edge or corner adsorption is such as to suppress or render more obtuse the adsorbing edge or corner. The mechanism of the habit change, as in the experimental instance of edge and corner adsorption by a growing crystal of lead nitrate, mentioned earlier, appears to be by lowering the growth velocity of the edges and corners to such a value that one of the possible crystal forms residing in them can develop on the crystal.

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[1]Frondel, C., op. cit., pp. 3–5.

[2]A photograph of one of these specimens has been published by Whitlock (1933, Nat. Hist., XXXIII, p. 276).

[3]Woodward, J. 1729. An Attempt Towards a Natural History of the Fossils of England. London, I, p. 152.

Miscellaneous Occurrences

Incrustations of chalcopyrite and of pyrite that are selective upon the (111) and (100) forms, respectively, of galena cubo-octahedrons have been described[1] in which the super-crystallization appears to have initiated upon the edges of the galena crystals and to have gradually extended from the edges over the whole area of the incrusted faces with increasing deposition. Smyth[2] has described incrustation pseudomorphs of pyrite after pyrrhotite in which the pyrite has built up as pronounced ridges upon the edges of the original pyrrhotite crystals, and Maier[3] has figured an instance in which an anglesite crystal projects in parallel growth from a corner of a barite crystal. An oriented edge incrustation of topaz upon trapezohedrons of spessartite, from the Thomas Range, Utah, has been briefly described by Montgomery.[4] A crystal of zircon from Iron Mountain, New York, has been described by Whitlock[5] as having gray zones of hematite or magnetite dust symmetrically disposed along certain of its edges.

Fluorite crystals are frequently noted to be more intensely pigmented along the edges of the crystals or to have the edges outlined by a pigment of a different color. Brauns[6] has figured fluorite cubes of a yellow color the edges of which are marked by a line of violet color and also colorless octahedrons that are blue on the corners. Several similar instances were observed on specimens in the Museum collection. The interior segments or "growth pyramids" beneath the different growth forms of single crystals of fluorite are sometimes found to be unequally pigmented, or differently pigmented, as a result of the unequal adsorbing power of the different forms,[7] and a continuance of crystal growth in these instances of edge and corner coloration would probably also result in the appearance of a selectively colored modifying form on the adsorbing edge or corner.

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[1]Frondel, C. 1934. Amer. Min., XIX, pp. 322–323.
[2]Smyth, C. H. 1911. Amer. Jour. Sci., Ser., 4, XXXII, pp. 156–160.
[3]Maier, A. 1923. Zeits. Kryst., LVIII, p. 98, fig. 12.
[4]Montgomery, A. 1934. Amer. Min., XIX, p. 86.
[5]Whitlock, H. P. 1907. N. Y. State Museum Bull. 107, p. 86, Pl. VI, fig. 18b.
[6]Brauns, R. 1903. Das Mineralreich (translated by L. J. Spencer, London, 1912), p. 375, Pl. LXXI, figs. 2, 12.
[7]Frondel, C. 1934. Amer. Mus. Novitates, No. 758, p. 6.